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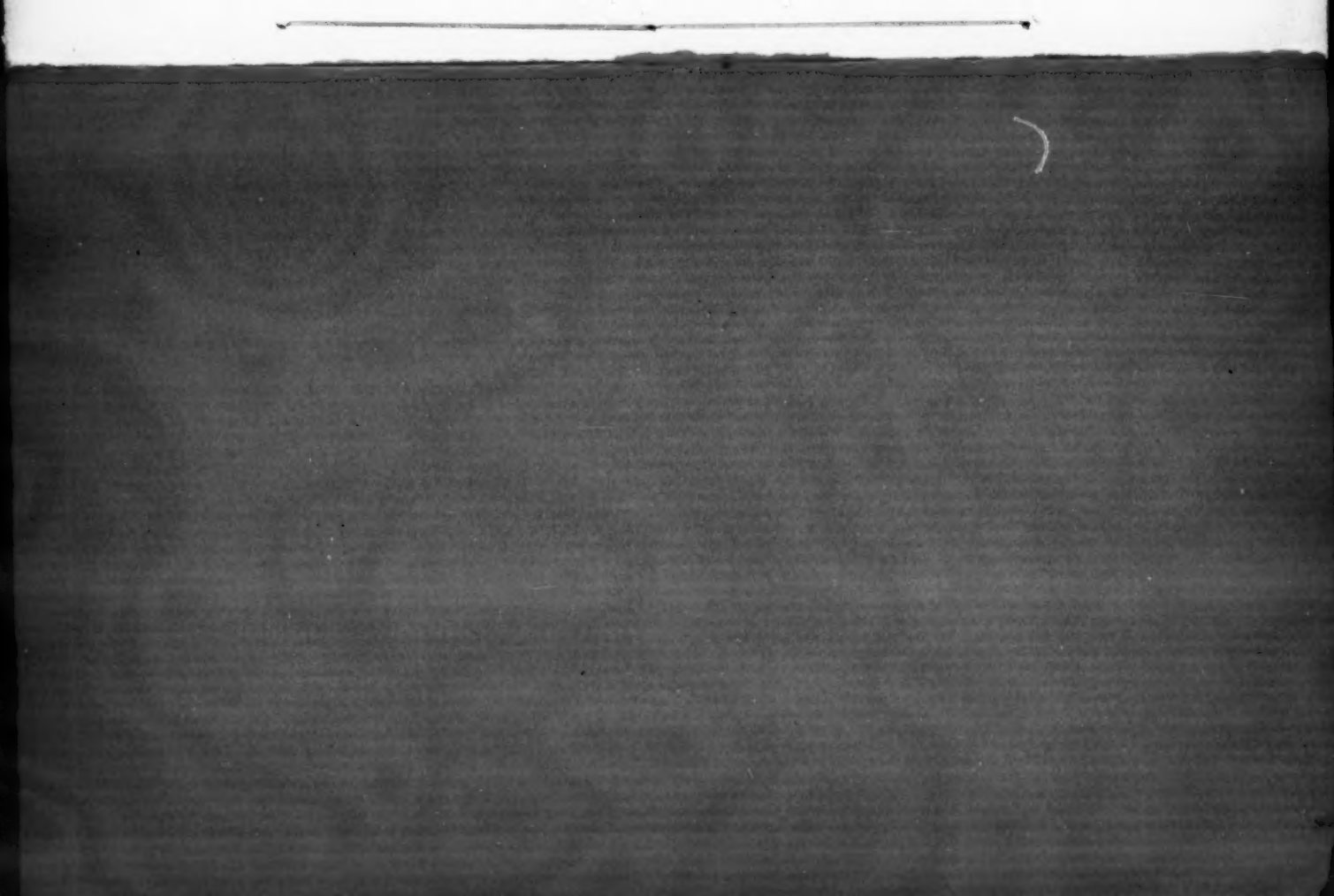

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A COMPARISON OF THE METHODS OF SEPARATION AND ESTIMATION OF ZIRCONIUM.

CHAS. BASKERVILLE.

The object of the research, whose results are recorded in this paper, was to compare some of the more prominent methods in use for the determination of zirconium. The directions, as found in the literature of the subject, were as closely followed as possible. At times however they were so indefinite that wide limits were given the analyst. In such cases, several experiments were carried out under varying conditions, so that the accuracy of the method might be fully tested.

It was further desirable in this work to examine any suggestion arising, by which a new method of determination might be devised and its accuracy as well tested. Whenever it seemed necessary the purity of the reagents was carefully proved.

Two solutions were used:

1st. A solution of zirconium chloride purified by crystallization from hydrochloric acid. This contained free acid.

2nd. A solution made by saturating dilute sulphuric acid (4:1) with zirconium hydroxide. This solution was acid to litmus.

The strength of each was determined by evaporating to dryness, igniting the residue and weighing the ZrO_2 obtained. Amounts taken for the experiments were measured from these solutions by means of a calibrated standard burette with a small outlet.

THE DETERMINATION OF ZIRCONIUM.

I. Experiments with Ammonium Hydroxide.

Ammonium hydroxide precipitated the zirconium completely from a cold solution in either a small or large excess. If the solution be hot, however, the excess of ammonium hydroxide must be boiled off, *i. e.*, the precautions taken when aluminium hydroxide is precipitated must be heeded. The precipitate is white and flocculent, settles quickly, is easily filtered and washed with hot water. In most of the experiments carried out this precipitate was washed until the wash water gave no further precipitate, or only a slight cloudiness, with silver nitrate. The precipitate was ignited and heated over the blast lamp until there was no further loss of weight, the residue weighed being taken as pure zirconium dioxide.

The following results were obtained:

Numbers.	*Found.*	*Used*
20	0.1082	0.1083
21	0.1624	0.1626
22	0.e081	0.1083
23	0.1618	0.1626
24	0.1098	0.1083
25	0.1647	0.1626
26	0.1090	0.1083
27	0.2812	0.2808
28	0.2832	0.2815

Nos. 20-26 inclusive were made from the chloride solution and Nos. 27-28 with the sulphate. No. 20 was carried out in the cold with a large excess of ammonium hydroxide. The solution was diluted to about 150 c.c. and the precipitate washed with cold water. No. 21 was also cold, the precipitate being obtained by ammonium hydroxide (sp. gr. 0.97) drop at a time. On addition of the fourth drop the precipitation was complete. No. 22 had also only a slight excess of ammonium hydroxide, but the zirconium was precipitated hot. No. 23 shows the necessity for boiling off the excess of ammonium hydroxide. It was precipitated from a hot solution by a large excess of ammonium hydroxide (10 c.c. sp. gr. 0.97). Nos. 24 and 25 respectively contained a slight and large excess of ammonia, but the boiling was continued for fifteen minutes in each case. No. 26 was diluted to about 100 c.c. (the others were diluted to about 150 c.c.) and 20 c.c. of concentrated ammonia water (sp. gr. 0.92) added and that boiled for fifteen minutes. No. 27 was carried out hot, the slight excess of ammonium hydroxide added being boiled until there was only a faint odor of it left. No. 29 was precipitated by adding 50 c.c. concentrated ammonia water (sp. gr. 0.92). The whole solution in this case amounted to about 100 c.c. This was boiled twenty minutes. Most of the ammonia had disappeared.

Since zirconium is frequently precipitated in a chloride solution when the alkaline chlorides are also present, it seemed advisable to note the effect the presence of these substances had on the determination by means of ammonium hydroxide. Experiments were therefore made with the zirconium chloride dissolved in ten per cent. solutions of ammonium, sodium, and potassium

chlorides. These solutions were at first clear, but on boiling 5—15 minutes, at first a slight turbidity was noticed. This increased on boiling until a good precipitate was formed. With potassium chloride this precipitate was curdy and incomplete. Paykull[1] speaks of the formation of double chlorides in the dry way. These precipitates which are very probably similar compounds are now being investigated in this laboratory. It was noted that ammonium chloride did not interfere with the determination, as it was easily volatilized when the crucible was ignited over the blowpipe. The fixed alkalies however interfered, giving high results. These compounds are of interest.

The following determinations were made in the presence of ammonium chloride:

Numbers.	*Found.*	*Used.*
59	0.1106	0.1104
30	0.1070	0.1070
31	0.1077	0.1070

II. With Sodium Thiosulphite.

Sodium thiosulphite, if added as solid crystals to a zirconium chloride solution, previously neutralized with ammonium hydroxide, and then boiled for several minutes, caused complete precipitation. The solid thiosulphite was added up to ten and even twenty per cent. of the solution. The precipitate did not form immediately on addition of the solid thiosulphite, even if the solution was hot, but was rapidly produced after a few moments heating. The precipitate, which settled quickly, was filtered hot and washed with hot water

(1) Ber. VI. 1467.

until the wash water amounted to about twice as much as the original solution. This amount of washing was arbitrarily chosen, as it was found that if it was considerably less the results ran high, showing imperfect washing, due to the presence of sulphite, no doubt. The presence of free acid (one per cent. and less) interfered considerably, preventing complete precipitation (39 and 40-*vid.* below). Moreover the precipitate was finely divided and ran through very close filter paper (S and S, No. 590) along with much free sulphur. The precipitation was made in the cold as well, but in that case, it was found necessary to let the solution remain covered for at least twenty-four hours with occasional stirring. The larger portion of the flocculent precipitate collected well at the bottom of the beaker, but a small portion clung persistently to the stirring rod and sides of the beaker, refusing to come off, even on the most vigorous rubbing with a "policeman."

This reagent will not serve as a precipitant for the zirconium sulphate solution, since the precipitation was found to be incomplete on addition of as much as twenty per cent. of solid sodium thiosulphite to a thoroughly neutralized solution. Preliminary experiments were made with more or less free sulphuric acid present and varying amounts of the thiosulphite (two to twenty per cent.) in solution and solid form, hot and cold.

These determinations were made:

Numbers.	*Found.*	*Used.*
33	0.1102	
34	0.1101	0.1104
35	0.1106	
36	0.1645	0.1635
37	0.1079	0.1104
38	0.1641	0.1635

39	0.0645	0,1104
40	0.1538	0.1635
41	0.1107	0.1104
42	0.1093	0.1104
44	0.1080	0.1083
45	0.1215	0.1296

Nos. 41 and 44 were carried out as first recommended above. Nos. 33 and 34 were in the cold, the former with one per cent., and the latter with three per cent. of sodium thiosulphite. No. 36 had also three per cent., but was boiled. No. 37 shows that a very small amount of sodium thiosulphite will throw down most of the zirconium, as only five drops of a ten per cent. solution were added in the experiment. The precipitation was complete on addition of the thiosulphite up to two per cent. (No. 38,) but the precipitate crept and only a portion settled well. Nos. 39, 40 and 42 show the varying interference of free hydrochloric acid, and No. 45 was a neutralized sulphate solution with twenty per cent. of solid sodium thiosulphite.

III. With Potatassium Sulphate.

The very old method for separation, which Berzelius[3] used for want of a better, and one recommended for use in a great number of text books now, is the precipitation of a zirconium sulphate solution as a basic zirconium potassium sulphate, which according to Paykull[4] may have the formula, $K_2SO_4.2[ZrO_2.Zr(SO_4)_2]+14H_2O$. This would be best brought about by adding an excess of a saturated potassium sulphate solution to a neutralized concentrated solution of zirconium sulphate. The pre-

3. Pogg. Ann. III-208.
4. Ber. VI-1467, and XII-1719.

cipitation however was incomplete even in neutral solutions. The text books vary in regard to the properties of this double sulphate; some[5] state the precipitate to be insoluble or sparingly soluble in either water or hydrochloric acid; another[6] states its solubility in water alone and points out the danger of loss in the necessary washing. Rose[7] referring to Berzelius[8] avoids this loss by washing with dilute ammonium or potassium hydroxide. These contradictory properties were all noted in Watt's Dictionary.

An experiment was carried out to learn the actual deportment of this salt in the presence of water. A fairly concentrated solution of zirconium sulphate, containing ten per cent. of ZrO_2, was completely neutralized with ammonium hydroxide until a permanent precipitate was formed and this dissolved in two or three drops of dilute sulphuric acid. This was done with a boiling solution. To this was added an excess of a saturated potassium sulphate solution. The beaker was placed in cool water. When cold the supernatant liquid, the flocculent precipitate having settled well, was decanted through a tared filter. This filtrate, was tested with more potassium sulphate, boiled and cooled, but no further precipitation occurred. On addition however of some ammonium hydroxide a white precipitate was thrown out, showing either that the potassium sulphate did not precipitate the zirconium completely or the precipitate was soluble in water. The precipitate was washed several times by decantation and the filtrate in each case showed the solubility of the salt.

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5. Roscoe and Schorl. vol. II, part II-p. 271., and Regnault Chimie II-285, and Wöhler Handbüch Anorg. Anal. p. 117.
6. Pelouse et Fremy Traité de Chimie Générale III-523 2nd Ed.
7. Analyt. Chem. translated by Griffin.
8. Poggendorff's Annalen, IV.-136.

There remained to learn the completeness of the precipitation, Another experiment similar to the above was carried out bearing in mind the suggestion of washing with a solution of ammonium hydroxide, at first with potassium sulphate to be sure that there was an excess of that reagent present and then with ammonium hydroxide. The precipitation had not been complete. After several washings, when the original solution might well be presumed to be removed, or the major portion at least, the wash water (very dilute ammonia water) gave no evidence of the presence of zirconium. Several experiments were carried out, but in only one case was the double salt weighed. It gave about ninety per cent. of the zirconium really present. The filtrates from several were examined and it was learned that from one to ten per cent. was always lost, the amount depending on the exact conditions of precipitation and the amount of washing succeeding. The objection to using ammonium hydroxide as wash water when it was desirable to separate zirconium from iron, aluminium or titanium, is easily seen.

The conclusion arrived at was, that the precipitation of zirconium as a double sulphate with potassium afforded no quantitative means of determination for that metal, nor of separation from aluminium, iron or titanium.

IV. By Sodium Carbonate.

Sodium carbonate precipitated solutions of zirconium salts completely. A great difficulty arose, however, in the exceeding slowness of filtration and practical impossibility of washing the precipitate free from the alkaline carbonate. A single result, obtained from several analyses, was

	Found.	*Used.*
ZrO_2	0.1785	0.1723

V. By Ammonium Carbonate.

When a saturated solution of ammonium carbonate was added gradually to a zirconium chloride solution, at first a white flocculent precipitate was thrown down. This seemed to be produced by the free ammonia present, but on a further addition the solution became clear again. If this was boiled, a clear flocculent precipitate came down. The boiling was continued for about fifteen minutes, when the carbon dioxide had ceased to come off. The appearance of this precipitate was exactly that produced by ammonium hydroxide, yet the filtration was very slow, as in the case with the other alkaline carbonate. In some hundred and more precipitations by means of ammonium hydroxide, I have never failed to secure the zirconium hydroxide in such a condition as to filter rapidly. This was very likely a basic carbonate, which required continued heat with the blow pipe for constant weight. Such a precipitate when ignited gave 0.1733 g. ZrO_2 when 0.1723 g. was used.

VI. By Ammonium Oxalate.

L. Svanberg,[9] because oxalic acid failed to give a complete precipitation of zirconium, thought the solution contained a new element, which he called *norium*. Sjögren[10] in his analyses of the mineral catapleiite said; " Eine nicht saure Lösung der Erde aus dem Katapleiite

9. Ofversigt of R. V. Akad. Förhandl. 1845, p. 37.
10. Pogg Ann. 1852, Ergänzung, III. p. 469. J. Prak. Ch. 55, 298.

wird wohl von oxalsaurem Ammoniak gefällt, aber dieser Niederschlag lösst sich nicht nur in einem Uberschusse des Fällungsmittels, sondern auch in einem geringen Zusatz von Oxalsäure." Berlin,[11] however, also said: "* * * dass der durch dieser Salz (ammonium oxalate) in einer Lösung von Zirkonerde bewirkte Niederschlag bei einem Ueberschusse des Fällungsmittels wieder verschwindet. * * * Aus dieser Auflösung schlägt Ammoniak die Zirkonerde vollständig nieder." Hermann[12] repeated all previous experiments, and not only corroborated Berlin's observations, but determined the best conditions for this precipitation. He noted that in an excess of the precipitant (ammonium oxalate), only four-tenths of all the zirconium was precipitated. Such has been the result of my own experiments, save the determination of the rate of precipitation as done by Hermann.

VII. By Potassium Hydrogen Oxalate.

Behrens(13) in his "Contributions to Micro-Chemical Analysis" notes that zirconium can be detected with extreme delicacy (0.0005 m.gr.) by that means. For quantitative purposes, however, potassium hydrogen oxalate could not be used, as the precipitate formed was soluble in an excess of the precipitant, but an incomplete precipitation took place on boiling.

VII. By Hydrogen Peroxide.

(See Separation Zirconium and Titanium.)

IX. By Sulphur Dioxide.

Because of the analogy of the elements, I was led to

11.. J Prak. Ch. 58—145.
12. J. Prak. Ch. 96—332.
(13) Zeit. Anal. Chem. translated in Ch. News, XLIV—124.

try a method commonly used with titanium, viz.: prolonged boiling of a potassium hydrogen sulphate fusion in dilute solution with sulphur dioxide in excess. On application of this method, however, on the prepared sulphate (see above), I failed even after boiling four hours with an excess of sulphur dioxide, to obtain a precipitate, if the solution was acid. If the solution was nearly neutralized with ammonium hydroxide, and then boiled with an excess of sulphur dioxide, after being greatly diluted a precipitate was produced. This precipitation, however, was incomplete, even after boiling six hours or passing steam through the same for two or three hours. The precipitate too was very finely divided, running through the closest filter papers at my command. Therefore this method could not be used.

But on addition of sulphur dioxide to the chloride solution, even in the cold, and if it was acid, a dense white precipitate was immediately noted. On boiling with an excess of sulphur dioxide in a neutralized solution, *i. e.*, the chloride solution, neutralized by ammonium hydroxide until the slight precipitate was no longer dissolved by boiling, and this precipitate then taken up with two or three drops of dilute dydrochloric acid, the separation of the zirconium was complete.

The accuracy of this method is shown by the following results:—

Number.	*Found.*	*Used.*
81	0.1074	0.1077
81	0.1078	
82	0.1043	0.1038
83	0.1070	0.1077
84	0.1047	0.1050

The precipitation took place immediately an addition of sulphur dioxide and after two minutes boiling the precipitate settled quickly and was easily filtered.

This method then is applicable to the chloride only and a sulphate would have to be first changed to chloride by precipitation with ammonium hyhroxide and resolution in hydrochloric acid. This was done and 0.2815 g. ZrO_2 was found when 0.2812 g. was used.

The presence of large amounts of such salts as ammonium chloride did not aid the precipitation of the sulphate. The presence of free hydrochloric acid must be avoided and it is best to use a fresh solution of sulphur dioxide or the gas direct.

SEPARATION OF ZIRCONIUM FROM IRON.

I. By Ammonium Sulphide in an Ammoniacal Tartrate Solution of their Salts.

Rose[14] knew the property tartaric acid possesses of rendering solutions of a number of metallic oxides incapable of precipitation by alkalies. However he made use of just such a solution, by adding to it an excess of ammonium sulphide, to separate iron from zirconium. He said, "If to the solution of these two bases a *sufficient* quantity of tartaric acid has been added, the addition of an excess of ammonia produces no precipitate. "I found five times as much tartaric acid as iron present was a "sufficient quantity," but an excess, five per cent. of the whole solution, had no ill effect, although such a large excess is not necessary. If the iron was present in the same amount as the zirconium, the separation was found to be incomplete, if only one precipitation of

14. Analyt. Chem. translated by Griffin, p. 58.

the iron was made. The zirconium dioxide could not be obtained perfectly white, but possessed from a yellow to a brown color due to the iron present. However, if the amount of iron be small, five per cent. and less, as it occurs in the mineral zircon, the separation was thorough and the ignited zirconium dioxide obtained was snow white and iron free.

Two analyses are given :—

	Found.	*Used.*
ZrO_2—	0.1119	0,1118
	0.2815	0.2818

The process was as follows: To the solution of the salts, tartaric acid, best solid, to five times the amount of iron present, was added, and this neutralized by an excess of ammonium hydroxide, and then ammonium sulphide in excess. This was warmed slightly, covered, and set aside to settle. The supernatant liquid must acquire a yellow color before filtration. To avoid this delay, one experiment was carried out by boiling and direct filtration. Time was thereby saved. The precipitated iron sulphide was washed quickly with a dilute ammonium sulphide solution. The filtrate was evaporated in a porcelain dish on a water bath until it became of small bulk, when it was transferred to the crucible, in which the final residue was to be weighed. Sometimes it was noticed that there was a further separation of iron sulphide during this evaporation. This was filtered off before the concentration became too great without causing any error in the final result. The crucible when apparently dry was heated for several hours in an air bath at 100 °C. and then ignited, top on. After the volatile portion of this residue was driven off, the lid was removed and all the carbon burned away.

The crucible was then heated with the blow pipe until the weight was constant. This required at least an hour if a porcelain crucible was used.

The method was carried out by the writer as given above and accurate results, as noted, obtained, when the iron was no more than five per cent of the two metals present. The iron was not determined. The great amount of time required was the only objection to be noted.

II. By Ammonium Hydroxide, Ammonium Sulphide and Sulphurous Acid.

Berthier[15] said that if a mixture of the salts of iron and zirconium in solution be precipitated by an excess of ammonium hydroxide and then an excess of ammonium sulphide be added, that the ferrous sulphide formed could be dissolved out with a sulphurous acid solution. Several experiments were carried out. The solution was precipitated by an excess of ammonium hydroxide, —in one the excess was boiled away—then an excess of freshly made ammonium sulphide was added and the whole allowed to settle. (Experiments were made with both the colorless and yellow ammonium sulphide). The supernatant liquid was drawn off, or the whole filtered, and the precipitate boiled with a strong sulphurous acid solution. Most of the black sulphide became immediately decolorized. After a five or ten minutes boiling, the solution was filtered and washed with hot water and a weak sulphur dioxide solution. The precipitate remained brown however, strongly colored by the iron which had not been dissolved. In one experiment this impure precipitate was redissolved

15. Booth's Encycl. Chem.

in dilute hydrochloric acid and the process repeated. There was only a slight diminution in the amount of iron left. If the hydrochloric acid solution of this precipitate was neutralized by ammonium hydroxide and then an excess of sulphurous acid added, the zirconium separated out perfectly white and free from iron.

	Found.	*Used.*
ZrO_2—	0.1070	0.1070

The method of Berthier as I carried it out did not give satisfactory results.

III. By Sodium Thiosulphite.

With proper precautions zirconium was completely separated from iron by means of sodium thiosulphite. The directions given for this method were not always specific.[16] It was noted (by the writer) that unless the solution be neutralized, the precipitation would be incomplete; also if it be neutral and the boiling long continued, the precipitate might be very finely divided and hard to catch on the filter paper; also if all or the greater part of the sulphur dioxide be boiled away the oxide of iron separated immediately on access of the air after the removal of the clock glass used to cover the beaker. No accurate separation was obtained if the solution was rendered neutral with ammonium hydroxide or the precipitation was made when the solution was hot.

But the method of Chancel[17] and Stromeyer[18] gave accurate results. By this method the solution was rendered neutral with sodium carbonate, the beaker

16. Rosc. and Schorl. II—sI—271., and Miller's Chem. II—p. 643.
17. Ann. Ch. Pharm. CVIII 237.
18. *Ibid*, CXIII-127.

placed in cold water, and when the solution was cooled, an excess of sodium thiosulphite was added. After the solution became decolorized, it was boiled, and the white precipitate (zirconium hydroxide according to Stromeyer) settled out well. This precipitate was easily filtered, washed with hot water, burned and ignited to constant weight.

These results are reported:—

Numbers.	*Found.*	*Used.*
140	0.1315	0.1333
141	0.0552	0.0565
143	0.1640	0.1614
145	0.1613	

Nos. 140 and 141 were in solutions in which there was present free acid—No. 140 hydrochloric—and No. 141 sulphuric. No. 143 was not properly neutralized and on addition of the sodium thiosulphite, a heavy flocculent flesh-colored precipitate settled out. This on warming became white, but when the precipitate was burned showed the presence of some iron. No. 145 was carried out exactly according to the directions given above.

IV. By Ammonium Sulphite.

As I carried out the experiments, I failed to succeed in perfectly separating iron and zirconium by this method, which is also recommended by Berthier.[19] Solutions of the chlorides of these two metals were made with equal and varying amounts of each, then an excess of freshly prepared ammonium sulphite was added. The zirconium sulphite precipitated was soluble in an

19. Booth's Encycl. Chem. 1850.

excess of the precipitant, but zirconium hydroxide was thrown down on boiling. If the boiling was kept up until no more sulphur dioxide came off, immediately on permitting the liquid to come into contact with the air, a scum of oxide of iron formed. Next, the boiling was not continued so long—the precipitate when burned, however, still contained some iron. Besides the results obtained were low, as may be seen by these analyses:—

Number.	*Found.*	*Used.*
150	0.0463	0.0535
152	0.0871	0.1070
156	0.0453	0.0535

The hydroxide is, doubtless, partly soluble in an excess of the sulphite, even after boiling.

V. By Sulphur Dioxide.

The method of precipitation of zirconium from a chloride solution on addition of sulphurous acid in excess affords an excellent means of separating zirconium from iron. The zirconia precipitated by sulphur dioxide in large excess and boiled two to three minutes, was, after filtration, washed four or five times with hot water. The further necessary precautions have been given above. The iron was titrated in the filtrate.

The experiments gave these results.

Number.		*Found.*	*Used.*
160	ZrO_2	0.1047	0.1043
	Fe	0.0830	0.08225
161	ZrO_2	0.1074	0.1070
	Fe	0.08248	0.08225
162	ZrO_2	0.1078	0.1070
	Fe	0.0820	0.08225

163	ZrO_2	0.1043	0.1043
	Fe	0.04389	0.04225
166	ZrO_2	0.0537	0.0535
	Fe	0.04334	0.04225

SEPARATION OF ZIRCONIUM FROM ALUMINIUM.

I. By Sodium Hydrogen Carbonate.

Having noted the property of zirconium of being re-precipitated from a solution (at first precpitated but soluble in an excess of sodium hydrogen carbonate) on boiling with ammonium chloride, Pelouse and Frémy[20] proposed it as a method of separation of that metal from aluminium. Severale xperiments were carried out by the author of this paper, but the conclusion arrived at was that it was a qualitative separation, which could not be used for quantitative purposes.

II. By Sodium Iodate.

Davis[21] gives a neat and accurate method for the separation of zirconium and aluminium. The directions, as given by him, for the process must be most carefully followed in order to obtain accurate results. Moreover the process is inapplicable when iron, be it in a ferrous or ferric condition, is present. The method therefore offers but little of practical value in ordinary analysis.

"Their[22] (aluminium and zirconium) solution in hydrochloric acid is treated with sodium carbonate until a permanent precipitate is formed. This precipitate is

20. Traité de Chimie Générale, III-523, 1854 Edition.
21. Am. Ch. J., XI-26.
22. *Ibid.* p. 29.

dissolved in the smallest possible quantity of dilute hydrochloric acid and sodium iodate ($NaIO_3$) added in excess. The solution is heated for about fifteen minutes. It is then allowed to stand twelve hours filtered, washed down with boiling water, dissolved in hydrochloric acid and finally precipitated with ammonia, ignited and weighed." I found in an analysis 0.0515 g. ZrO_2 when I had used 0.0520 g.

Analyses were made also according to his recommendation of the use of from five to ten per cent. of sodium chloride. The results obtained were high, doubtless due to imperfect washing. An example:

	Found.	*Used.*
ZrO_2	0.0596	0.0520

The numerous experiments made served merely to confirm Davis' work. It was necessary to avoid a too far neutralization with sodium carbonate as the separated zirconium was contaminated with varying amounts of aluminium. The permanent precipitate formed by the sodium carbonate was difficult at times to redissolve in a small amount of dilute hydrochloric acid. Yet an excess of acid must be avoided, for it was learned by experiments, as Davis had noted, that the presence of even 0.1 per cent. by weight of hydrochloric acid would cause low results. Four hours was a sufficient time for complete separation however. An experiment with the sulphate solution showed no action whatever. Even the small amount of sulphuric acid in an aluminium sulphate solution was found to interfere, hence the necessity of having a hydrochloric acid solution, free from sulphuric acid, was apparent. Davis evidently noted this as he was particular in having a pure solution of aluminium chloride in his experiments.

III. By Sulphur Dioxide.

Sulphurous acid may be used for the separation of zirconium and aluminium as well. The process is essentially the same as for the separation of iron and zirconium (see above).

The analyses proving this are also given.

Number.		*Found.*	*Used.*
201	ZrO_2	0.1042	0.1043
	Al_2O	0.0608	0.0610
207	ZrO	0.1070	0.1070
	Al_2O	0.0316	0.0305

SEPARATION OF ZIRCONIUM AND TITANIUM.

As is well known, titanium and zirconium are metals possessing many properties in common. Their deportment with reagents is very similar, varying only in degree, as a rule. This fact, and that of the properties of each being further altered by the presence of the other in the same solution,[23] renders their separation extremely difficult. An example of this alteration of properties was noted on boiling a solution of sulphates of these metals. On long continued boiling titanium sulphate, when in solution alone, is completely precipitated. Zirconium sulphate, under the same conditions. produces no precipitate, whereas a mixture of these permits of only a partial precipitation of the titanium, the larger portion remaining undissolved (Berzelius[24]).

I. By Potassium Sulphate.

It was not found possible to use the precipitation of

23 Rose Analyt. Chem, p. 172.
24. Pogg. Ann. VI., 232.

the zirconium as the basic potassium sulphate, for the reasons above noted. For want of a better method, however, this was for a long time used.

II. By Boiling an Acetic Acid Solution.

Franz and Streit claimed complete separation if the solution, neutralized by ammonium hydroxide, were rendered strongly acid with acetic acid and boiled sometime. The usual preliminary qualitative experiments were carried out by the writer, and he obtained a precipitate in both cases. The titanium was precipitated directly and in large amounts, whilst the zirconium was also precipitated, but in small amounts. Of course solutions of approximately known strength were used in these experiments. When this was noted the completeness of the titanium precipitation was not tested. This method, therefore could not be recommended.

III. By Ammonium Oxalate and Ammonium Carbonate.

The experiments of Hermann[25] were very carefully repeated. The zirconium chloride solution was diluted to contain one part in one hundred parts of water, and to this was added double the weight (of zirconium) of ammonium oxalate. I did observe, as he says,[26] "Dabeienstand anfänglich eine Trübung, nachdem aber die ganze Quantität des Oxalats zugesetzt worden war, klärte sich die Flüssigkeit wieder vollständig auf. Man

25. J. Prak. Ch. 97—338.
26. *Ibid*, 337:

gass jetzt diese Lösung von oxalsaurer Ammoniak-Zirkonerde in eine concentrirte Lösung von kohlensaurem Ammoniumoxyd." But I did *not* observe, "Dabei blieb die Flüssigkeit ganz klar und setzte auch nach längerem Stehen keine Spur eines Niederschlags ab."

A chloride solution of titanium, treated in the same manner as above, gave a heavy precipitate, when the double oxalate formed an addition of the ammonium oxalate, was poured into a saturated solution of ammonium carbonate. As noted above a precipitate was obtained with the zirconium chloride solution as well; nevertheless an analysis was made and 0.0327 g. titanium was found when 0.0302 g. had been used. This proved to the writer that advantage could not be taken of this for a *complete* separation of zirconium from titanium. Hermann[27] noted this incompleteness in his further remarks concerning an experiment he performed: "Die geringe Differenz von 0.18 Theilen Zirkonerde zu wenig und 0.18 Theilen (used 6, found 6.18) Titansäure zu viel kam daher, dass die Titansäure beim Fällen durch kohlensaures Ammoniumoxyd ein geringe Menge Zirkonerde mit niedergerissen hatte."

IV. By Hydrogen Peroxide.

So no good and accurate method was known until Bailey[28] noted the effect of adding hydrogen dioxide to a zirconium solution. This is the only thoroughly accurate method yet proposed. Its neatness and rapidity in application are to be especially noted. At the same time consideration must be given to the difficulty in obtaining perfectly pure hydrogen dioxide.

27. *Ibid*, 439.
28. J. London Ch. Soc. Trans. 1886, p. 149.

He proceeded[29] by adding an excess of hydrogen dioxide to a moderately acid solution of a mixture of iron, zirconium and titanium. After twenty-four hours standing in a stoppered flask, the precipitated oxide (Zr_2O_5) was caught and filtered, washed and ignited. In carrying out this method the writer noted the necessity of having an acid, yet not too acid, solution. If the solution was first neutralized with ammonium hydroxide or sodium carbonate, the precipitated zirconium oxide was highly contaminated with iron, which could not be washed out.

Analyses gave these results:

Numbers.	*Found.*	*Used*
ZrO_2	0.1111	0.1118
Fe	0.0135	0.0138
TiO	0.0302	0.0302
ZrO_2	0.2425	0.2424

The precipitation was found to be complete on boiling the solution two or three minutes to avoid the twenty-four hours delay by standing cold. After filtering from the zirconium oxide, the filtrate was rendered alkaline with ammonia water, filtered and the precipitate dissolved in dilute hydrochloric acid. The excess of acid was neutralized and the titanium determined by precipitation on boiling with sulphur dioxide.[30] The iron was determined from the filtrate from this.

The hydrogen dioxide obtained from the manufacturer[31] was found to contain a large amount of silicic acid in solution along with the other ordinary impuri-

29. *Ibid* p. 482.
30. The author J. Am. Ch. S.
31. Dr. Merchand, 28 Prince st., New York.

ties. The strength of this solution was 72 volumes, being brought to this strength according to Thénard's method[32] (Marchand). I further purified and concentrated this to 111 volumes by distilling in partial vacuum, according to Talbot and Moody.[33] I found the potassium sulphate present interfered very much with the reaction by the formation of the more or less soluble basic zirconium potassium sulphate. So nothing definite could be learned from my experiments, which were many, with either the 111 or 72 volume hydrogen peroxide.

To avoid the formation of the compound with potassium sulphate, hydrochloric acid[34] was used. By this method was obtained a solution of the dioxide practically free from silicic and sulphuric acids, but one weaker, being only 55 volumes. It was with this solution the analyses above reported were made.

This method of using hydrogen dioxide is the only accurate method given for the separation of zirconium and titanium. It is direct and rapid, delicate and elegant, but expensive and by no means always convenient.

I cannot close this summation without expressing my great indebtedness to Dr. F. P. Venable, for his ever ready sympathy with and kindness to me in this work. I wish also to express my thanks to Dr. Chas. Marchand, 28 Prince st., New York, for six pounds of 72 volume hydrogen peroxide, with which he kindly presented me.

33. Mass. Inst. Technology Quarterly, V-123.
34. *Ibid*, 131.
32. Anneles de Chemie de Physique, [2] 10-114, 335, 11-85.

PRIMITIVE STREAK AND BLASTOPORE OF THE BIRD EMBRYO.

BY H. V. WILSON.

Embryologists, with but few exceptions, recognize in the bird embryo a gastrula stage. There is, however, a very considerable diversity of opinion as to just what constitutes the gastrula. Leaving aside certain interpretations for which at present there seems no good ground, we find there are two very different views held regarding the nature of this embryonic stage.

According to the older view, advanced by Balfour and Rauber, the essential difference between the bird gastrula and the fish gastrula is that a part of the original edge of the blastoderm, is in the bird turned in to form the primitive streak. Thus while in the fish the blastopore is represented by the blastoderm edge, in the bird it is represented by the primitive streak plus the blastoderm edge. This theoretical view receives the support of the well known researches of Duval on the germ layers of birds[1]. Duval finds that the very young blastoderm of the bird is similar to that of fishes. In both, the ectoderm and entoderm are continuous round the edge, which therefore corresponds to the blastopore. But this precise similarity is only transient, for in the bird the primitive streak soon makes its appearance. The manner in which the primitive streak is formed proves conclusively that it is only a modified part of the blastoderm edge. The young blastoderm (fish-like stage) grows centrifugally at all

1. De la formation du blastoderme dans l'oeuf d'oiseau. Annales des Sciences Nat. Zoologie. T. XVIII.. 1884.

points except at that which corresponds to the future tail end of the embryo. By this means a certain portion of the blastoderm edge becomes turned in on each side of the median line in the posterior region, the two portions running forwards side by side to the point already mentioned, where no centrifugal growth occurs. These two portions fuse and form the primitive streak, which thus at first extends to the very edge of the blastoderm. Now, however, centrifugal growth begins at the posterior pole of the blastoderm, and the primitive streak gradually takes up its well known position at a distance from the edge.

In opposition to this view Oscar Hertwig, Rabl, and others claim that the blastoderm edge is not a part of the gastrula mouth, but is a peculiarity of certain mesoblastic ova, and that the blastopore is represented exclusively by a structure known as the *sickle* plus the primitive streak. This doctrine is based on the belief that an ingrowth or invagination of cells takes place only in the region of the sickle and streak, and not round the edge of the blastoderm. In a paper on the development of teleost fish I have already attempted a criticism of this view[2], and will only add that it is to my own mind in direct contradiction with the admirable account given by Duval of the formation of the primitive streak. On the other hand it receives support from the discoveries of Kupffer on the reptilian embryo, and from Koller's description of the way the streak is formed in the bird embryo.

According to Koller's account[3], which is adopted by

2. The Embryology of the Sea Bass. Bulletin U. S. Fish Commission. Washington. 1891, pp. 268–271.

3. Beiträge zur Kenntniss des Hühnerkeims in Beginne der Bebrütung. SB. der König. Akad. d. Wiss. Wien. 1879.—Untersuchungen über die Blätterbildung in Hühnerei. Archiv für Mikros. Anat. Bd. XX. 1881.

Hertwig in his text book, there very early developes a sickle-shaped thickening which lies between the area pellucida and the area opaca, in the posterior region of the blastoderm. A groove, the sickle groove, is present in this thickening, and in the median line there is a short anterior projection called the *sichel-knopf*. The primitive streak is produced by the continuous growth in the median line, of the *sichel-knopf*, and is therefore an outgrowth of the sickle. Since neither the sickle nor the primitive streak is at any time connected with the blastoderm edge, the latter structure cannot be regarded as a part of the blastopore, which is represented exclusively by the two former structures.

The contradiction between Duval's and Koller's account concerns a fundamental feature of the process of gastrulation, and more facts on the early history of the bird blastoderm are much to be desired. Duval himself, in his criticism of Koller's papers (l. c.), states it as his opinion that the sickle is an inconstant feature, of no morphological importance, belonging in the same category as other local thickenings of the blastoderm. I may mention that I have myself looked through very young blastoderms, in which the primitive streak was from one-half to two-thirds the length of the area pellucida, without discovering in the majority of them any trace of the sickle. I am aware that Koller describes the sickle as becoming much less conspicuous with the continued growth of the streak, but his figures of blastoderms[4] corresponding in age to mine, show an evident remnant of the sickle, while I can find no trace of such a structure in the majority of my embryos.

Koller, it will be remembered, kept his eggs at a

4. SB. d. König. Akad. d. Wiss. 1879, Beitrag. &c., figs. IV.a. IV.b. V.

temperature below the normal temperature of incubation, in order to lessen the rapidity of development. A certain percentage of abnormalities was to have been expected from the use of the temperature below the normal, and I have satisfied myself that at 35° various kinds of abnormalities do occur. Out of a considerable number of young blastoderms, incubated at 35°, while the majority showed no trace of the sickle, in a few cases the primitive streak exhibited abnormalities suggesting more or less strongly the sickle. Surface views of two of these blastoderms are given in Figs. 1 and 2. In the primitive streak of Fig. 2, I could not make out the primitive groove, but the groove was very evident in the sickle at the posterior end of the streak. (Kupffer and Benecke[5] give a wood-cut figure of a chick blastoderm, quite like my figure 2, except that the primitive groove is shown. While they incline to the belief that the sickle in such a blastoderm is of morphological importance, they admit that it was only rarely that such blastoderms were found.) In the blastoderm shown in Fig. 1, the groove was conspicuous, both in the streak and in the transverse outgrowths of the streak. This blastoderm was sectioned longitudinally. A median section through the streak is shown in Fig. 3. The transverse groove is deep; the hypoblast is differentiated as a distinct layer; the epiblast and mesoblast are indistinguishably fused. In Fig. 4 is represented a section lying in the plane *x-y* of Fig 1. In this region the transverse groove is as deep as in the median section, but the three layers are separate.

My failure to find the sickle in blastoderms where, according to Koller it should be present, and the obser-

5. Die ersten Entwicklungs vorgänge am Ei der Reptilien. Königsberg. 1878. p. 11.

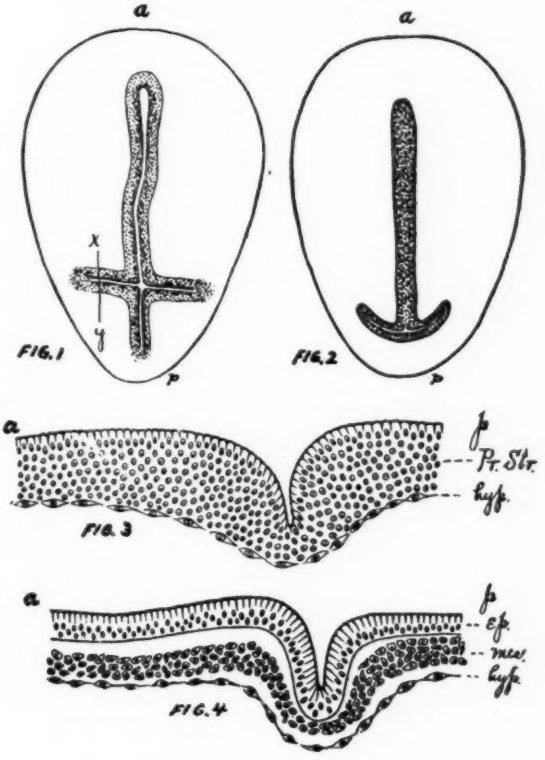

FIG. 1

FIG. 2

FIG. 3

FIG. 4

vation of abnormalities resembling in a measure the sickle, incline me to accept Duval's view of this structure, and with him to regard it as an inconstant feature of no morphological importance.

Hertwig, in his paper on "*Urmundrand Spina bifida*," (1892), touches on the question of meroblastic gastrulation, and it would seem that he no longer believes in the existence of Koller's sickle. For in his brief sketch of the manner in which the primitive streak is formed, he follows Duval, and represents the streak as arising by the coalescence the blastoderm edges. He therefore comes to regard the edge of the young blastoderm as the blastopore.

Hertwig does not look on the entire edge of the young blastoderm as the blastopore, but for some reason unknown to me divides it into a blastoporic part and a part designated as the *Umwachsungsrand*, by which name he formerly (text-book) meant the entire blastoderm edge. The edge of the teleost blastoderm is likewise divided into blastopore and *umwachsungsrand*. This division is surprising, for round the entire edge of the teleost blastoderm there is an ingrowth of cells, just as there is round the blastopore lip of the amphibian embryo. And the existense of such an ingrowth is undoubtedly a very strong argument for regarding the whole edge as the blastopore. It would be interesting to learn the facts that have induced Professor Hertwig to divide the edge of the teleost blastoderm in this manner.

But if Hertwig has come to regard the edge of the blastoderm, or any part of it, as representing the *urmundrand* in the bird embryo, it would seem that he must have abandoned his former views on gastrulation

in the Sauropsida, and have taken a long step towards the position of Balfour and Rouber.

CHAPEL HILL, NORTH CAROLINA.

Explanation of the figures illustrating Mr. Wilson's paper on "Primitive Streak and Blastopore of the Bird Embryo":

Fig. 1. Surface view of abnormal chick blastoderm. + 16.

Fig. 2. " " + 16.

Fig. 3. Median longitudinal section through the primitive streak of Fig. 1. × 90.

Fig. 4. Longitudinal section through line x-y of Fig. 1. × 90.

a.—anterior.
p.—posterior.
ep.—epiblast
mes.—mesoblast.
hyp.—hypoblast.
Pr. str.—primitive streak.

ADDITIONS TO THE ERYSIPHEÆ OF ALABAMA.

BY GEO. F. ATKINSON.

In Vol. VII, II, of this Journal was published a list of the Erysipheæ, collected by the writer, from the Carolinas and Alabama. During the following year several more species were collected in Alabama by the writer and one of his students. The former list was accompanied with quite full notes of a descriptive character. In the present list only such notes are added as seem necessary in addition to the characterizations found in descriptive works:

Sphærotheca castagnei Lev.

On Erectites hieracifolia, Nov. 5, 91; and Bidens frondosa, Nov. 3, 91, B. M. Duggar, collector.

S. lanestris Hark.

On Quercus alba, Dec. 91, G. F. A. The conidial stage only was found.

Erisiphe cichoraceurum D C.

On Helianthus annuus, Oct. 19. 91, B. M. D. Aster tradescantia, Nov. 31; A. diffusus, Nov. 30; Mikania scandens, Oct. 26. and Solanum carolinense, Nov. 10, 91, G. F. A.

E. galeopsidis D C.

On Verbena urticifolia, Oct. 23, 91, B. M. D.

E. liriodendri Schwein.

On Liriodendron tulipifera, Oct. 28, 91, B. M. D.

Phyllactinia suffulta (Reb.) Sacc,

On Cornus florida, Nov. 3; Cornus sp. undtd, Oct. 18.

Podosphæra biuncinata C. & P.

On Hamamelis virginiana, Oct 28, 91, B. M. D.

P. oxacanthæ (DC).

Prunus americanus var. mollis, Oct. 31, 91, B. M. D; Cratægus, Nov. 9, D. H. Benton.

Microsphæra semitosta B. & C.

Tecoma radicans, Oct. 19, 91, G. F. A. This species has heretofore been reported only on Cephalanthus occidentalis. The perithecia are a little larger than those I have observed on Cephalanthus, measuring 90 to 115. The appendages in well matured specimens are very characteristic.

M. euphorbiæ B. & C.

On Euphorbia preslii, Oct. 21, 91, B. M. D.

M. ravenelii B.

On Gleditschia tricanthos, Oct. 13, 91, G. F. A.

M. vaccinii C. & P.

On Vaccinium, Oct. 18, 91, B. M. D.

M. grossulariæ (Wallr.).

On Sambucus canadensis, Oct. 13, 91, G. F. A. In the previous list this occurred as was given as M. vanbruntiana Ger.

The measurements are given in terms of the micro-millimeter.

BOTANICAL DEPARTMENT, CORNELL UNIVERSITY.

SOME SEPTORIÆ FROM ALABAMA.

BY GEO. F. ATKINSON.

The species of Septoria enumerated in this list were collected during my connection with the Alabama Polytechnic Institute at Auburn, Ala. The list is not large, perhaps from the fact that no especial effort was made to collect the members of the genus. Where no name is given as collector they were collected by myself. Where no locality is given Auburn should be understood.

Septoria brunellæ E. & H.

On Prunella vulgaris, July 16, 90, Shorters. The specific name of this plant was given from a mistaken spelling of the genus Prunella which has crept into many American botanical works. See Coville, Bot. Death Valley Expedition, p. 176.

S. cerastii Rob. et Desm.

On Cerastium arvense, Mar. 25, 91. Perithecia not very black, probably because they are not very old. The spores are a little stouter than the description calls for, and are faintly 1 – 5 septate. The spores in the

specimen in Roumg. Fung. Gall. Exs. 2485, are also faintly 1 – 5 septate; the perithecia are very black but agree with the Alabama specimens in being rather angular in outline.

S. rubi West.

On cultivated Rubus, Aug. 8, 90.

S. rubi var alba Peck.

On Rubus trivialis, Apr. 91, Mobile, Zimmer Bros. The leaves are also affected with Cercospora rubi West. and Caeoma nitens.

S. virgaurae Desm?

On Solidago seratina. There is some doubt about the correct determination of this plant. It seems near this species, but the spores measure 30 – 40 and are faintly 3 – 5 septate. Perithecia small 50 – 75. Spots small, whitish, depressed, dark bordered.

S. erechtites E. & E.

On Erechtites hieracifolia, Sept 10, 91, B. M. Duggar.

S. œnothera West.

On Œnothera biennis,

S. dianthi West.

On Dianthus barbatus,

S. specularia B. & C.

On Specularia perfoliata, Mar 28, 90.

S. jussiæa E. & K.

On Jussiæa leptocarpa, July 24, 91, Duggar and Newman.

S. sambucina Pk.

On Sambucus canadensis, Aug 24, 91, B. M. D.

S. sonchina Thüm.

On Sonchus oleraceus, Feb. 25, 91, B. M. D.

S violæ West.

Viola primulæfolia, July 16, 90, Shorters.

S. xanthii Desm.

On Xanthium, July 11, 90, Uniontown.

S. graminum Desm.

On Panicum sanguinale, Aug. 19, 91, B. M. D. Spots brown, elongate, irregular or involving the larger part of the terminal portion of the leaf. Perithecia amphigenous, more abundantly epiphyllous black, frequently depressed when dry, 80 – 90. Spores hyalines, slender, larger at base, soon tapering into a long, very slender, strongly curved flagellum, 2 – 10 septate. Very young ones are narrowly obclavate with the smaller end little curved and 1 – 2 septate, 1 – 1½ in diameter at base, 30 – 70 long.

S. alabamensis n. sp.

On Nepeta glechoma, Jan. 29, and Feb. 27, 91. Spots indefinite, occupying irregular portions of the leaf. Perithecia 80 – 90. Spores 20 – 30 x 1 or less, sometimes faintly 1 – 3 septate, staight or slightly curved or flexuous.

The measurements are given in terms of the micromillimeter.

Botanical Department, Cornell University.

ADDITIONAL NOTE ON THE FUNGI OF BLOWING ROCK, N. C.

In making out the list of fungi from Blowing Rock, which was published in Part 2, Vol. IX, of this Journal, two species were overlooked. They are as follows:

Cordyceps acicularis Rav.

On larva of elaterid beetle.

Cnomoniella coryli (Batsch.) Sacc.

On leaves of Corylus.

Geo. F. Atkinson.

AN EXAMINATION OF THE CHLORIDES OF ZIRCONIUM.

BY F. P. VENABLE.

A chloride of zirconium of definite composition would prove a valuable compound for determining the atomic weight of the element. There are several difficulties in the way of securing such a result:

1. The tendency to form basic chlorides.
2. The ease with which hydrochloric acid is lost through the action of heat and of dehydrating agents.
3. The presence of free hydrochloric acid.
4. The deliquescent nature of the chlorides.

It is particularly desirable that the conditions under which a definite chloride can be formed should be discovered, as zirconium seems to yield no very satisfactory compounds for the determination of the atomic weight. There have been many efforts at finding out these exact conditions.

Most text-books state that anhydrous, pure zirconium tetra-chloride can be prepared by passing dry chlorine over a mixture of charcoal and zirconia heated to a high temperature. Hermann used this sublimed zirconium chloride for the determination of the atomic weight. As Clarke says, however, little confidence can be placed in his results. Bailey* has recorded that even with great care to avoid the presence of moisture, he was unable to prevent the formation of oxychlorides. He also says that in no case was it found possible to prepare the chloride free from iron and silica. The

*Chem. News. LX.. 17.

necessity for the presence of these in the materials used or in the resulting compound is not very apparent. I have as yet had no opportunity of repeating his experiments.

The chlorides most commonly worked with have been those formed by the solution of the hydroxide in hydrochloric acid, followed by precipitation or crystallization from concentrated hydrochloric acid.

Berzelius attempted to remove the excess of hydrochloric acid by heating the salt to 60° C. but was not able to obtain a definite compound. Two analyses gave:

ZrO_2	0.332	0.485
AgCl	0.661	1.076

The silver chloride should be about two and one-third times as much as the oxide.

Paykull dried the salt between filter paper and found the composition of the crystals to be $ZrOCl_2$. $8H_2O$, the amorphous form precipitated by hydrochloric acid being $2ZrOCl_2$. $13H_2O$.

Endemann has described basic or oxychlorides $Zr_3O\,Cl_4$; ZrOClOH, and $Zr_8O_8Cl_7(OH)_9$; Troost and Hautefeuille have described others, $Zr_2O_3Cl_2$ and Zr_2OCl_6. In fact water is so easily taken up and hydrochloric acid lost that a large number of such indefinite compounds might be prepared by slightly varying the conditions.

Nylander* made a series of attempts at dehydrating the chloride. He prepared the chloride by dissolving the hydroxide in hydrochloric acid and evaporating to crystallization. The salt formed white needles, easily

*Bidrag till kinnedomen om Zirkonjord. Inaug. Diss. Lund 1864.

soluble in water. They were washed with alcohol and for analyses I. and II. were pressed between filter paper. III. and IV. were dried over sulphuric acid. The results were as follows:

Zr	27.56	95.69	30.11	31.78
Cl	21.58	21.58	23.06	23.80
Loss (H_2O)	50.86	52.78	46.83	44.12

or calculated on a dry basis:

Zr	56.08	54.41	56.63	57.18
Cl	43.02	45.59	43.37	42.82

Again preparations were made as before. I. was dried between filter paper, II. over sulphuric acid, III. was pressed between filter paper and then dried over sulphuric acid, IV. was dried a long time over sulphuric acid. The analyses gave the following:

Zr	28.52	34.91	37.78	35.69
Cl	21.93	26.09	25.87	21.74
Loss	49.55	39.10	36.35	42.57

or calculated on a dry basis:

Zr	56.93	57.23	59.34	62.14
Cl	43.07	42.77	40.66	37.86

Lastly he allowed a solution of the chloride to evaporate over sulphuric acid, washed the crystals obtained with alcohol and pressed them between filter paper. Analyses gave:

	I.	II.
Zr	27.94	28.74
Cl	27.32	26.67
Loss	44.74	42.62

or, calculated on a dry basis:

Zr	50.36	50.04	Zr	38.50
Cl	49.44	49.96	Cl_4	61.50

The above results show that his preparations were indefinite oxychlorides or mixtures, in varying proportions of zirconium tetrachloride and oxychloride.

Bailey repeatedly crystallized the chloride from hydrochloric acid, washed it with hydrochloric acid and then removed the free acid.

1. By washing with a mixture of one part alcohol and ten parts of ether.

2. By gently heating the salt.

3. By exposing the finely divided salt at ordinary temperatures in a vacuous dessicator over potash, until no hydrochloric acid appeared when air passed over it.

The analysis was performed by dissolving the salt in water and precipitating the zirconia with ammonia, then acidulating with nitric acid and precipitating the chlorine by means of silver nitrate. By method 2 a constant and progressive diminution of chlorine was observed. Therefore no analyses were made. For the other methods he gives the results of the analyses by a statement of the ratio of ZrO_2 to AgCl:

	ZrO_2 : AgCl
Berzeliu's determination	1 : 1.991
	1 : 2.260
Bailey's method 1:	1 : 2.206
	1 : 2.179
	1 : 2.226
	1 : 2.260
Method 2:	1 : 2.264
Method 2 without washing:	1 : 2.245
	1 : 2.309
	1 : 2.285
$ZrOCl_2$	1 : 2.350

These preparations are evidently mixtures, also.

Hermann* states that the hydrated chloride, gotten in crystals on evaporating its aqueous solution, becomes opaque at 50° C., giving off part of the water and half of the hydrochloric acid, and leaving a basic chloride or oxychloride, $ZrCl_4.ZrO_2.\ 18H_2O$ or $ZrOCl_2.9H_2O$. The same compound is obtained in stellate groups of white silky prisms on evaporating a solution of the chloride. These crystals, when heated, become white and turbid and are converted into the anhydrous dioxychloride $ZrCl_4.2ZrO_2$.

The conditions here are inexact, and though Hermann may have obtained these compounds, he would find it difficult to prepare them again. While it is perfectly true that an oxychloride is formed on the evaporation of an aqueous solution of the chloride, I have been unable to obtain the compounds he mentions. Linnemann† maintains that crystallization from hyhrochloric acid (sp. gr. 1.17) and treatment with alcohol and ether gives a fine, crystalline, snow white, silky body, leaving 50 per cent. of its weight on ignition, and therefore very nearly pure $ZrCl_4$ which should leave 52.5 per cent. He claims that this is "chiefly a neutral, not a basic compound."

My own experiments on the dehydration of this salt have extended over the past two years, as opportunity was afforded. Several series of experiments were undertaken; some along the lines attempted by others, and others by methods not tried before. In all the purified chloride, obtained by repeated crystallization from hydrochloric acid was used, the salt being still wet with

*Watts Dict. V. p. 180.

†Chem. News. LII. 224.

the excess of the acid. There was no attempt at drying this between filter paper. The method of preparing this salt has been fully described in a previous paper in the *Journal of Analytical and Applied Chemistry*, 5, 551.

In the first experiment this chloride was washed once with water and then put in a dessicator and dried over calcium chloride (porous dessicated). It remained in the dessicator about seven months. Even after this lapse of time it still continued to show a slight loss in weight. It yielded, on analysis, 48.84 per cent. ZrO_2.

Another portion was placed in a jar over solid lumps of sodium hydroxide. After six weeks the loss was very slight. Careful ignition left a residue of ZrO_2, equivalent to 42.99 per cent. of the original weight. There was found to be 24.44 per cent. of chlorine present.

Again a portion was placed over calcium chloride and dry air was drawn over it at the rate of about fifty litres in the twenty-four hours for six months. After the first two months it was examined weekly by the interposition of a flask containing silver nitrate to see whether hydrochloric acid was still coming off. Even after the lapse of so long a time as this it was found that the loss of hydrochloric acid continued, although it was slight. On analysis this gave ZrO_2 42.28 per cent. and Cl. 24.35. Although the results in this, and the experiments immediately preceding, correspond fairly well they are unsatisfactory, as they point either to a mixture of chlorides or an oxychloride of very complicated formula, and hence unsuited for the ultimate aim of the research.

Lastly a portion was placed over concentrated sulphuric acid and the atmosphere above it exhausted occa-

sionally. This was kept up during two months of summer weather. The loss in the last fifteen days was about .02 per cent. of the whole. The mass was powdery, with a slightly discolored crust. It was all soluble in water, however, and yielded a clear colorless solution. It contained 53.30 per cent of ZrO_2. This corresponds very nearly to the formula $ZrCl_4$ and is altogether at variance with the results obtained by Nylander and with the assertion made by Hermann, that half of the hydrochloric acid was lost over sulphuric acid.

This last experiment showed the possibility of securing pure zirconium chloride, provided the excess of hydrochloric acid could be removed. It was thought that this might be done by heating in an atmosphere of hydrochloric acid. A weighed flask was so arranged that it could be kept at a definite temperature while a stream of dry hydrogen chloride was passing through it. The temperature ranged from 100° to 110° C. and the chloride placed in the flask melted, solidifying again after the loss of the water and excess of hydrochloric acid. If the drying was done slowly enough fine crystals of zirconium chloride were gotten which lost no further weight on being kept at 100° C. A more rapid drying left a hard white mass which was quite hygroscopic. Heating this mass for several days did not cause any diminution in weight, provided the flask was kept full of hydrogen chloride. If the mass was heated even a short time in the absence of hydrogen chloride then further heating caused a continuous loss of weight even in the presence of a rapid stream of hydrogen chloride. After this it was impossible to secure a constant weight.

This method of drying has been tried repeatedly on

various preparations, and I regard them as showing conclusively that a neutral chloride of zirconium can be prepared and dried.

Analyses of this chloride gave the following percentages of ZrO_2:

52.70	52.78	52.63

Experiments have already been begun with a view of utilizing this body in a series of experiments looking to a revision of the atomic weight of zirconium.

In connection with this subject it may be well to mention some improvements in the method of purifying zirconium chloride. (See *Journal of Analytical and Applied Chemistry*, 5, 551).

In the first place the separation from silica by evaporation to dryness is not complete. It is impossible to heat this chloride to the necessary temperature without such a decomposition as will render the zirconium chloride also insoluble. It is best then to make this preparation as thorough as possible by heating, then to change the chloride into oxide by ignition, and to treat this several times with hydrofluoric acid until the trace of silica is all driven off. This silica is too small in amount to interfere with ordinary uses but would have to be removed where perfect purity was demanded.

Again, where the hydroxide is dissolved in dilute hydrochloric acid, or contained so much water that the acid was greatly diluted by it, it will be found that more or less of a white insoluble powder will form on evaporation as recommended on a water-bath and on subsequent treatment with boiling strong hydrochloric acid. By a careful arrangement of glass wool in a hot water funnel the dissolved chloride can be filtered

away from this soluble mass. It seems to be quite insoluble in hydrochloric acid though easily dissolved by water. Analysis shows that this mass is $ZrOCl_2$ and with it was found as an impurity whatever silica the separation by heating failed to remove.

Lastly, my assistant, Dr. Baskerville. has shown that much time and hydrochloric acid will be saved if in the solution containing much iron the zirconium hydroxide be first precipitated out by means of sulphur dioxide. This precipitate can then be dissolved in acid and purified by crystallization as already recommended.

Of course it need scarcely be mentioned that if silica has been removed by ignition and treatment with hydrofluoric acid, it will be necessary to fuse once more with caustic alkali and repeat the ordinary purification.

UNIVERSITY OF NORTH CAROLINA.

SOME ATTEMPTS AT THE FORMATION OF ETHYL GLUCOSIDE.

J. R. HARRIS.

Glucosides are substances ocurring in nature in plants and are supposed to be ethereal derivatives of the glucoses. Under the action of dilute acids or ferments they break up into glucose and other bodies. A number of these ethereal derivatives of glucose can be prepared synthetically in the laboratory.

A. Michael[1] obtained them by the action of alcoholic solution of acetochlorhydrose upon the alkali salts of phenol.

1. Compt. rend. 89, 355.

The formation of Helicin according to the following equation would be an example of this method: $C_6H_7ClO_5(C\ H_3O)_4 + C_7H_3O_2K + 4C_2H_6O = C_{13}H_{16}O_7 + KCl + 4C_2H_5C_2H_3O_2$.

Emil Fischer[2] has recently discovered a new method of forming these derivatives. and has prepared compounds of methyl, ethyl, propyl, amyl, isopropyl, allyl and benzoyl glucose. Also analogous compounds of arabinose, methyl-arabinoside.

These do not reduce Fehling's solution; they break up into glucose and the corresponding alcohol on treatment with dilute acids or ferments, and behave in every way similarly to the natural glucosides.

I proposed to form them by the action of alkyl iodide upon the sodium glucosate according to the following equation:

$$C_6H_{11}NaO_6 + C_2H_5I = C_6H_{11}O_6.C_2H_5 + NaI.$$

For this experiment, the ethyl glucoside was chosen, as the materials for its preparation were already on hand, and because in all probability the method would work as well for this one as any other member of the series.

The insolubility of sodium glucosate in all neutral anhydrous mediums on hand, was recognized at the outset of this work to be a great obstacle in the way of the successful operation of the method.

As a preliminary test, 15 grs. of anhydrous glucose was taken and gently boiled for some time with 150 c. c. of about 97 per cent. alcohol. This solution, when saturated, was poured off into a large flask in which the precipitation was to be made, and kept warm by standing in a water bath, in order to prevent the glucose from crystallizing.

2. Ber. 26, 2400.

Another portion of 150 c. c. of alcohol was poured upon the residue and gently boiled as before. When the hot alcohol seemed no longer to have any solvent action upon the residue, it was carefully decanted off into the precipitating flask.

About half the amount of glucose taken went in solution by this treatment.

The alcoholic solution was then precipitated with an excess of sodium alcoholate, and allowed to stand over night. An amount of ethyl iodide equivalent to the sodium alcoholate used was then added direct to the alcoholic solution containing the suspended precipitate of sodium glucosate. The mixture was now gradually warmed up on a water bath, with a reflux condenser attached to prevent loss of ethyl iodide.

At about 75° C. the mixture began to deposit a reddish brown substance upon the bottom of the flask, and the solution to change to yellow color. At about 80° C. the mixture boiled, and the deposition on the bottom of the flask was more rapid, it being complete in about twenty minutes, leaving a dark brown supernatant liquid. A portion of the liquid was taken out and allowed to stand for some time over freshly ignited potassium carbonate, but no absorption of iodine was noticed.

This, and the remaining portion in the flask, was then filtered through animal charcoal. A liquid of a pale brown color was obtained, which reduced Fehling's solution.

It was not thought that the change would be complete, so it was impossible to tell by this means whether or not the glucoside had been formed. It was then evaporated in a water bath to a syrupy consistence, and the syrup extracted several times with acetic ether.

The acetic ether extract was evaporated in a dessicator over sulphuric acid.

By this means beautiful crystals were obtained, however, colored somewhat by the brownish syrup.

These crystals were tested by the flame test for sodium, and starch paste for iodine. They were clearly shown to be sodium iodide.

The glucose used in this experiment was thought to be impure, and besides it was probable that another test, under somewhat different conditions, would give more satisfactory results.

In his work on glucosides, Fischer[3] dissolves the glucose in a little water, and besides, water is formed in the reaction which he made use of, hence I concluded that it was not absolutely essential for the materials used to be water free. I accordingly started another experiment, using pure anhydrous glucose[4] of my own preparation dissolved in a little water.

Fifteen grams of glucose was dissolved in 5 c. c. of hot water and the solution added to 300 c. c. of 98 per cent. alcohol. This solution was precipitated by an equivalent amount of sodium alcoholate. The precipitate was rapidly filtered off by means of a pump, exposed to air as little as possible, washed with 98 per cent alcohol and transferred to the precipitating flask.

The precipitate was now suspended in 300 c. c. 98 per cent alcohol and an amount of ethyl iodide added equivalent to the sodium ethylate. The mixture was now carefully heated up on a water-bath, with frequent shaking.

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3 Ber. 26, 2400.

4. Made by the method of Soxhlet J. pr. ch. 21, 245, as given in Emil Fischer's book on Organic Preparations, and purified by recrystallization from strong alcohol.

It was noticed that the change began to take place as before, at about 70° C., by the brownish deposit at the bottom and sides of the flask, as the flask was this time immersed in hot water, taking care that the mixture should not come to boiling.

The greater portion collected on the bottom as a dark brown semi-syrup at that temperature, and the supernatant liquid was straw colored.

The change was complete on heating for 30 minutes just below the boiling point of the mixture. The liquid in the flask now had a strong smell of ethyl iodide, and reduced Fehling's solution.

About half was poured into a smaller flask provided with a reflux condenser and gently boiled in a water bath for three hours. At the end of this time the smell of the ethyl iodide did not seem to have diminished, and it still reduced Fehling's solution.

It was then evaporated on a water bath to a syrupy consistency, and the syrup extracted with a mixture of equal parts alcohol and ether, benzen, petroleum ether and acetic ether. No crystal of sodium iodide could be obtained, and only a thick syrup which powerfully reduced Fehling's solution.

The other portion of the liquid was then transferred to a distilling flask and fractioned. A few c. c. came over between 74° and 78° C. and was mainly C_2H_5OH. Most of the alcohol comes over between 78° and 82° C., leaving a dark brown syrup behind in the flask. The dark brown substance obtained as a deposit in the operation was set aside for examination. Meanwhile another experiment was started, varying the conditions somewhat.

Fifteen grams of anhydrous glucose was dissolved in 400 c. c. boiling absolute alcohol. The solution

cooled somewhat, and an equivalent amount of sodium ethylate added, and rapidly cooled to the same temperature. The precipitate was filtered off by means of pump and washed with absolute alcohol, avoiding all exposure to the air possible. It was then transferred to the precipitating flask and an equivalent amount of ethyl iodide added.

The mixture in the flask provided with a reflux condenser, was gradually warmed up to boiling. The changes first noted were the formation of a dark brown deposit on the bottom of the flask at about 70° C., a coloring of the liquid, and at the same time a diminution of the precipitate. Finally, at the boiling point of the mixture, the precipitate appeared to become sticky, and to collect into one mass, instead of being flocculent, and to gradually get smaller and smaller, both going into solution and coloring it a dark brown and melting down to a semi-syrup on the bottom of the flask.

The, time, in this test, for the change was one hour; much longer than in the former experiments. The liquid in the flask was divided into two portions, one of which was boiled in a flask with a reflux condenser for several hours, and no change was observed.

It reduced Fehling's solution and had a strong smell of ethyl iodide. The portions were now combined and submitted to fractional distillation.

About half of the amount of ethyl iodide used was recovered in the fraction coming over between 74° and 78° C.

The alcoholic fraction emitted still a strong smell of the iodide. Hence it seemed that the ethyl iodide had played no part in the change undergone by the sodium glucosate. The residue left in the flask from the experi-

ment was treated with benzen, ether, petroleum ether and chloroform, but none of these had any appreciable solvent action. It was then dissolved in water, a portion of the solution evaporated to dryness in a platinum dish, dried to constant weight, and then ignited at a low red heat.

Weight of dish and substance, - -	24.9115 gr.
Weight of dish, - - - - - - - -	23.8732
Weight of substance taken, - -	1.0383
Weight of ash and dish, - -	24.1276 gr.
Weight of dish, - - . -	23.8732
Weight of ash, - - - -	2644

To ash, 34.50 per cent.

This was recognized as sodium carbonate, and is equivalent to 10.63 per cent sodium.

The percentage of sodium calculated for sodium glucosate is 11.37 per cent.; found in this syrup 10.63 per cent. Hence it must be a modification of glucosate.

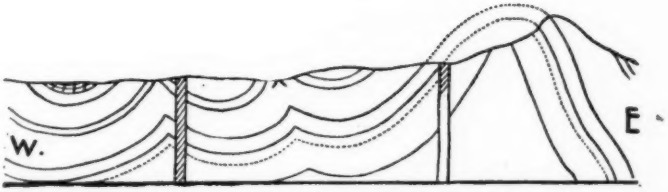
In conclusion it is hardly necessary to say that the negative results of the above experiments do not prove the impractibility of the reaction proposed. It remains, however, to find some neutral anhydrous medium in which sodium glucosate is soluble and by which it is not decomposed, as in most chemical reactions of this character the reacting bodies must be either liquid or in solution.

ON THE GEOLOGICAL HISTORY OF CERTAIN TOPOGRAPHICAL FEATURES EAST OF THE BLUE RIDGE.

COLLIER COBB.

The peculiar forms of the topographic outliers of the Blue Ridge, extending across North Carolina from King's Mountain on the south to Pilot Mountain on the north, attracted my attention when a boy, and in May, 1892, I visited the region and began a study of the King's Mountain district under the direction of Professor N. S. Shaler. The entire summer was spent on the field, as well as the larger portion of the following summer and two of my winter vacations.

The precipitous faces of the mountains, lying at two well-marked levels, suggested to me wave action, and I began my work upon the hypothesis that these outliers had been islands in a sea of no great depth, at a date comparatively late, when the age of the rocks composing the mountains is taken into consideration. The accompanying geological section, from what was formerly known as Bird's Quarry, in the present village of King's Mountain, westward across the mountain, I have adapted from Lieber, putting in the quartzite which forms the crest of the mountain, lying above Lieber's "mica slate." The order of succession of these rocks is, beginning with the newest, limestone, talc-schist, a white sandstone passing into a slightly flexible variety, micaceous shale, diorite-schist, talc-schist, quartzite, and micaceous shale, the last resting on a granitic rock which outcrops on Crowder's creek at the eastern foot of the mountain.



SECTION EAST AND WEST THROUGH KING'S MOUNTAIN.

[There is a marked unconformity between the limestones and the schists not shown in Lieber's section.]

King's Mountain, Crowder's Mountain, and the hills to the north on the old Lincolnton road, are the western members of a southward plunging syncline while the hills to the east of High Shoals, Dallas and Gastonia, are the eastern members, the same hard crest making the crest of them all. On the eastern side of the syncline the dip to the west is not great, averaging not more than fifteen degrees; while the eastward dip on the King's Mountain side is usually between thirty degrees and forty-five degrees. The eastern hills are low, rising very little above the surrounding country, which varies little from nine hundred feet above tide, and they show none of the topographic features so prominent on the western side, where King's Mountain rises to a height of 1692 feet, and Crowder's Mountain 1606 feet. The level of nine hundred feet is a base-level of erosion, clearly marked, and extending entirely across the State, from north to south, and just above "the fall-line" to the base of the Blue Ridge mountains.

The evidences of wave action upon and at the base of these cliffs is clear and unmistakable. They consist of sea-caves, pinnacled rocks—many of the Devil's Pulpit type—washed-out dykes, crevices of the spouting horn sort, below which may even yet be made out the old beaches which lay below the cliffs. These wave-markings are shown in the photographs of various portions of King's and Crowder's mountains. These features are nearly all on the west side, the side away from the dip. The best marked of these old sea-benches varies little from 1400 feet above sea-level. The next one that can be made out distinctly at all points is about 1000 feet above sea.

I then made a search for the fragmental material that

had accumulated during the island existence of these mountains. There is a good talus all around, rather more on the eastern side, where it is shingly, than on the west. A search for the stratified deposits immediately around the mountains was not at first so successful; but in the cut of the Charleston, Cincinnati and Chicago railroad, at Blacksburg, S. C., just back of the Cherokee Inn, is a very good exposure showing two or three feet of quartzite pebbles covered with about the same thickness of mottled clay closely resembling the Miocene clays of eastern North Carolina. Later, I found the same strata of quartzite pebbles and clays in the old cutting at the Catawba Gold Mine, about one mile from the mountain, and also pebbles, clays and regular stratified sands in a basin like region on the road from All Healing Springs to Gastonia, two miles southwest from Gastonia. The general absence of these deposits, however, is to be explained by their looseness, and the ease with which they could be washed away by the currents. The taluses have in every case, I think, been formed since the sea departed from the region, as the materials composing them are angular fragments, and never the round pebbles to be found in the deposits mentioned above. Not only have the deposits of this time been largely washed away, but the older crystallines, which are here decayed to great depths, have yielded readily to the rains wherever the land has been deforested. The accompanying photograph, taken on the Gastonia road two and a half miles from All Healing Spring, shows a gully twenty to thirty feet deep made by the rains since the Civil War when the field was abandoned. It may be noted that the trees which have come upon the field since its

abandonment are none of them more than thirty years old, as shown by their rings of annual growth.

I could find in the King's Mountain region no means of determining the approximate age of these deposits, but when I extended my observations across the State to the Dan River and Pilot Mountain regions, I found there the same pebbles of quartz and quartzite resting uncomformably upon the brown sandstones of the Newark system, while above the pebble-beds, and conformable with them, were the same mottled clays that I had found in the King's Mountain region. This established their date as certainly post-Triassic, and I should have been inclined to call them Cretaceous, had not an examination of the border of the Cretaceous in Harnett, Cumberland and Moore counties, convinced me by the coarseness of the materials there that there was the western border of the Cretaceous, and that the beds of that age could not have extended as far westward as the region under consideration. It led me to the belief, however, that the base-levelling of the piedmont region must have been accomplished while the shore-line lay near the present western border of the Cretaceous rocks, or in Cretaceous time. And, while I am as yet unable to determine the exact age of these deposits, I have at least found out that the peculiar shaping of these topographic outliers was the work of waves, and that it was accomplished in post-Cretaceous time.

DO SNAKES CHARM BIRDS?

COLLIER COBB.

On the 15th of May I happened upon an interesting thing which throws some light on the alleged power of snakes to charm birds. A few days before this, a snake, a garter (*Eutænia*), about the size of a man's finger and little over eighteen inches in length, had been killed in the walk leading from the New East Building to the eastern side of the University campus, at Chapel Hill. The head of the snake had been pushed into the hole made by the end of the cane with which it was killed, and the snake was in this position, with its head pressed down in the hole, when I came upon it, surrounded by seven quails (*Ortyx virginiana*). The quails were gazing upon the snake, very much as "charmed" chickens will gaze upon the chalk line or the crack in barn floor, taking no notice whatever of my presence until I lifted the snake up with a stick. They remained in the position in which I found them long enough for a boy to run from the Episcopal church to the walk, which must have taken two or three minutes. This observation is valuable as showing that, in this instance at least, the "charming" is in the bird itself, and is not a power possessed by the snake.